03-28-00

JC571 U.S. PTO
03/27/00

A

PATENT

Attorney's Docket No.: U 012676-7

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

JC564 U.S. PTO
09/537450
03/27/00

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of Inventors:

1. ASHISH KISHOR **LELE**
2. SHYNI **VARGHESE**
3. MANOHAR VIRUPAX **BADIGER**
4. RAGHUNATH ANANT **MASHELKAR**

WARNING: *The Declaration must name all of the actual inventor(s).*

For (title):
PROCESS FOR THE PREPARATION OF POLYMERIC ABSORBENTS

1. Type of Application

This new application is for a(n) (check one applicable item below):

☑ Original (nonprovisional)

☐ Design

☐ Plant

WARNING: ***Do not*** *use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. 371(c)(4) unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

CERTIFICATION UNDER 37 CFR 1.10

I hereby certify that this New Application Transmittal and the documents referred to as enclosed therein are being deposited with the United States Postal Service on this date **MARCH 27, 2000 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EL386268143US addressed to the: Assistant Commissioner of Patents, Washington, D.C.** 20231

GERALDINE MARTI
(type or print name of person mailing paper)

Geraldine Marti
(Signature of person mailing paper)

NOTE: Each paper or fee referred to as enclosed herein has the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 CFR 1.10(b).

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 CFR 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

EL386268143US

WARNING: ***Do not*** *use this transmittal for the filing of a provisional application.*

2. Benefit of Prior U.S. Application(s) (35 U.S.C. 119(e), 120, or 121)

NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. 120, 121 or 365(c). (35 U.S.C. 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

WARNING: *When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional* ***must*** *be filed prior to the Saturday, Sunday or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).*

☐ The new application being transmitted claims the benefit of prior U.S. application(s) and enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

☐ Divisional.

☐ Continuation.

☐ Continuation-in-Part (C-I-P).

3. Papers Enclosed That Are Required For Filing Date Under 37 CFR 1.53 (Regular) or 37 CFR 1.153 (Design) Application

14 Pages of specification

3 Pages of claims

1 Pages of Abstract

_ Sheets of drawing

☐ formal

☐ informal

WARNING: ***DO NOT*** *submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. Comments on proposed new 37 CFR 1.84. Notice of March 9, 1988 (1990 O.G. 57-62).*

NOTE: "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page." 37 C.F.R. 1.84(c).

(complete the following, if applicable)

☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)". 37 C.F.R. 1.84(b).

4. Additional papers enclosed

- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement (37 CFR 1.98)
- ☐ Form PTO-1449
- ☐ Citations
- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other

5. Declaration or oath

☐ Enclosed

executed by *(check **all** applicable boxes)*

- ☐ inventors.
- ☐ legal representative of inventors. 37 CFR 1.42 or 1.43
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
  - ☐ This is the petition required by 37 CFR 1.47 and the statement required by 37 CFR 1.47 is also attached. *See item 13 below for fee.*

☑ Not Enclosed.

WARNING: *Where the filing is a completion in the U.S. of an International Application but where a declaration is not available or where the completion of the U.S. application contains subject matter in addition to the International Application the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

☑ Application is made by a person authorized under 37 CFR 1.41(c) on behalf of *all the above named inventors.* (The declaration or oath, along with the surcharge required by 37 CFR 1.16(e) can be filed subsequently).

NOTE: It is important that all the correct inventor(s) are named for filing under 37 CFR 1.41(c) and 1.53(b).

☐ Showing that the filing is authorized. *(Not required unless called into question. 37 CFR 1.41(d).)*

6. Inventorship Statement

WARNING: *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.*

The inventorship for all the claims in this application are:

- ☐ The same
- ☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

7. **Language**

NOTE: An application including a signed oath or declaration may be filed in a language other than English. A verified English translation of the non-English language application and the processing fee of $130.00 required by 37 CFR 1.17(k) is required to be filed with the application or within such time as may be set by the Office. 37 CFR 1.52(d).

NOTE: A non-English oath or declaration in the form provided or approved by the PTO need not be translated. 37 CFR 1.69(b).

☑ English

☐ non-English

☐ the attached translation is a verified translation. 37 CFR 1.52(d).

8. **Assignment**

☑ An assignment of the invention to COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☑ will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

WARNING: *A newly executed "CERTIFICATE UNDER 37 CFR 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993. 1150 O.G. 62-64.*

9. **Certified Copy**

Certified copy of application

Country	**Appln. No.**	**Filed**

from which priority is claimed

☐ is attached.

☐ will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 CFR 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. 120 is itself entitled to priority from a prior foreign application then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. **Fee Calculation (37 CFR 1.16)**

A. ☑ Regular Application

Claims as Filed

Number Filed				Number Extra		Rate	Basic Fee 37 CFR 1.16(a) $690.00
Total Claims (37 CFR 1.16(c))	17	- 20	=	0	x $	18.00	
Independent Claims (37 CFR 1.16(b))	1	- 3	=	0	x $	78.00	
Multiple dependent claim(s), if any (37 CFR 1.16(d))					+ $	260.00	

☐ Amendment cancelling extra claims enclosed.

☐ Amendment deleting multiple-dependencies enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 CFR 1.16(d).

Filing Fee Calculation $

B. ☐ Design application
($310.00 — 37 CFR 1.16(f))

Filing Fee Calculation $

C. ☐ Plant application
($480.00 — 37 CFR 1.16(g))

Filing Fee Calculation $

11. Small Entity Statement(s)

☐ Verified Statement(s) that this is a filing by a small entity under 37 CFR 1.9 and 1.27 is(are) attached or has been filed.

Filing Fee Calculation (50% of **A**, **B** or **C** above) $

NOTE: Any excess of the full fee paid will be refunded if a verified statement and a refund request are filed within 2 months of the date of timely payment of a full fee. 37 CFR 1.28(a).

12. Request for International-Type Search (37 CFR 1.104(d)) ***(Complete, if applicable)***

☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made At This Time

☑ Not Enclosed

☑ No filing fee is to be paid at this time. *(This and the surcharge required by 37 CFR 1.16(e) can be paid subsequently.)*

☐ Enclosed

☐ basic filing fee $

☐ Recording assignment
($40.00; 37 CFR 1.21(h)) (See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION.")

☐ Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached.
($130.00; 37 CFR 1.47 and 1.17(h)) $

☐ For processing an application with a specification in a non-English language.
($130.00; 37 CFR 1.52(d) and 1.17(k)) $

☐ Processing and retention fee
($130.00; 37 CFR 1.53(d) and 1.21(l))

☐ Fee for international-type search report
($40.00; 37 CFR 1.21(e)). $

NOTE: *37 CFR 1.21(l) establishes a fee for processing and retaining any application which is abandoned for failing to complete the application pursuant to 37 CFR 1.53(d) and this, as well as the changes to 37 CFR 1.53 and 1.78, indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid or the processing and retention fee of §1.21(l) must be paid within 1 year from notification under §53(d).*

Total fees enclosed $

14. Method of Payment of Fees

☐ Check in the amount of $

☐ Charge Account No. 12-0425 in the amount of $

A duplicate of this transmittal is attached.

NOTE: *Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 CFR 1.22(b).*

15. Authorization to Charge Additional Fees

WARNING: *If no fees are to be paid on filing, the following items should not be completed.*
WARNING: *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.*

☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. 12-0425.

☐ 37 CFR 1.16(a), (f) or (g) (filing fees)

☐ 37 CFR 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: *Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 CFR 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.*

☐ 37 CFR 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)

☐ 37 CFR 1.17 (application processing fees)

WARNING: *While 37 CFR 1.17(a), (b), (c) and (d) deal with extensions of time under §1.136(a), this authorization should be made only with the knowledge that: "Submission of the appropriate extension fee under 37 C.F.R. 1.136(a) is to no avail unless a request or petition for extension is filed." (Emphasis added). Notice of November 5,1985 (1060 O.G. 27)*

☐ 37 CFR 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 CFR 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 CFR 1.311(b).

NOTE: 37 CFR 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application ... prior to paying, or at the time of paying, ... issue fee". From the wording of 37 CFR 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

16. Instructions As To Overpayment

☐ credit Account No. 12-0425

☐ refund

Signature of Attorney

Reg. No. 25,858

Tel. No. (212) 708-1945

William R. Evans
Ladas & Parry
26 West 61 Street
New York, NY 10023

☐ **Incorporation by reference of added pages**

(Check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added ___

☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added ___

☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added ___

☑ **Statement Where No Further Pages Added**

(If no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item:)

☑ This transmittal ends with this page.

PROCESS FOR THE PREPARATION OF POLYMERIC ABSORBENTS

Field of the invention

The present invention relates to a process for the preparation of polymeric absorbents useful for the gelling of organic liquids. More particularly, the present invention relates to a process for the preparation of polymeric absorbents which are cross-linked (5 to 50 %) and are capable of absorbing organic liquids in the presence of a ppm level metal additive. The polymers prepared by the process of the present invention have a proper balance of hydrophilic and hydrophobic character in its chemical structure. The polymers prepared by this technique are known in the art as polymer gels or more commonly and hereinafter referred to as gels.

Background of the invention

Polymer gels consist of cross-linked macromolecules that form a three dimensional network in which solvent molecules are absorbed by osmotic forces. Polymer gels have an equilibrium absorption capacity, which is governed by a balance of osmotic pressure of the solvent and the elastic stress of the network. Polymer gels, which absorb water, are referred to as hydrogels. Those hydrogels, which can absorb large quantities of water, such as in excess of 100 gram of water per gram of dry gel, are called superabsorbants. Polymeric superabsorbents have been widely used in personal care products such as sanitary napkins and diapers. They have also been used in agricultural applications such as for irrigating dry and arid land. Recent developments and new applications of superabsorbents have been outlined in literature (Bucholz, F. L., *Chemtech*, Sept. 38, (1994)). Superabsorbing gels are prepared by polymerising highly hydrophilic monomers such as acrylamide and acrylic acid along with a small quantity of multifunctional monomers and using a suitable initiator, typically a radical initiator, in water as a solvent.

Superabsorbing hydrogels do not absorb organic solvents. In fact, many of them collapse in organic solvents such as acetone and alcohol. Gels, which can absorb organic solvents, have been developed to a limited extent. Examples of such gels are chlorosulfonated polyethylene gels (Varma, A. J., Lele, A. K. and Mashelkar, R. A., *Chem. Engg. Sci.*, 50, 3835 (1995)) and polyethylene oxide gels (Graham, N. B., Nwachuku, N. E. and Walsh, D. J., *Polymer*, 23, 1345 (1982)).

There are several advantages of absorbing organic liquids into gels. For example, the liquid can be transformed into a soft solid by entrapping into a three dimensional matrix of a gel. Soft solids have typical properties that are intermediate between solids and liquids. For example, gelled organic liquids can have a high viscosity as well as a finite modulus. In general, gelled liquids find applications in pastes, lotions, creams, shampoos, oil drilling fluids and in fuels. Gelled fuels are particularly useful for cooking and chafing dishes. They are easier and safer to transport and are more effective owing to the slower diffusive release of the fuel from the gelled matrix. Such gelled fuels typically contain an alcohol, usually methanol or ethanol as the fuel, which may be mixed with other C_1 to C_6 alcohols. It is desirable to gel the fuel in such a manner that it does not separate from the matrix on standing or on application of pressure.

Alcohol based gels have been formed by different gelling agents. US Patent No. 3, 754, 877 discloses the use of olefin modified hydroxyalkyl cellulose as the gelling agent. US Patent No. 4, 436, 525 discloses the gelling of a 3:1 mixture of methyl alcohol and isopropyl alcohol with a fatty acid soap and sodium hydroxide. US Patent No. 3, 759, 674 discloses the dispersions of ethylene-acrylic acid copolymers and amine emulsifiers in water, which form gels when mixed with alcohols. These gels contain about 10 to 30 % by weight of solids. US Patent No. 3, 148, 958, US Patent No. 4, 261, 700 and US Patent No. 4, 365, 971 disclose the use of carboxy vinyl polymers

such as Carbopol ethylene acrylic acid copolymer partially neutralised by weak amines as gelling agents for alcohols. US Patent No. 5, 641, 890 discloses the use of an amine neutralised anionic polymer such as Carbopol 676 along with an amphoteric rheological additive such as dispersed alumina for gelling alcohol. The gel so formed contains about 20 to 30 % by weight of water. The gel is formed by non-covalent physical cross-links originating from interactions between the polymer and the amine. A typical gel contains about 70 weight % alcohol and about 1 weight % each of the polymer and the amine.

While the disclosures referred to above are interesting, they do not provide any teaching as to the structural features of the polymer absorbent. Also, no teaching is provided for synthesizing a solvent absorbing covalently cross-inked polymer gel. Whereas the disclosures of the above references have used a commercial polymer, in the present invention the polymer gel is prepared *in situ* by polymerizing selected monomers which contain a proper balance of hydrophilic and hydrophobic character in the presence or absence of a suitable transition metal compound. The proper choice of monomers containing hydrophilic and hydrophobic functional groups is particularly necessary for absorption of C_1 to C_6 alcohol and their mixtures, without the need for presence of water. Also in the prior art, the gels prepared inevitably required additional gels in order to increase the viscosity thereof.

The gel of the invention does not require any other gelling agents besides the polymer itself. The gelled fuels may or may not contain any water. Absence of water can significantly improve the burning characteristics thus giving an improved gel. Polymerisation of the monomer in the presence of a suitable transition metal compound helps in controlling the level of cross-linking reaction as well as forming structural complexes with the organic liquid. This improves the absorption capacity of the polymer for the organic liquid. The gel so prepared does not require any other gelling

agent or thickening agent to increase the viscosity besides the polymer unlike the disclosures of the above references.

Objects of the invention

It is an object of the invention to provide a polymer gel that can osmotically absorb large quantities of organic solvents to form gelled liquids.

It is another object of the invention to provide polymer gels that can be used for the formation of gelled fuels.

It is further object of the invention to provide a process for the preparation of polymer gels that can be used for preparing gelled fuels useful in cooking and heating food.

It is yet another object to provide polymer gels that do not require further gelling and/or thickening agents to increase the viscosity thereof.

It is a further object to provide a process for the preparation of polymer gels that have improved absorption capacity for organic liquids, particularly organic solvents.

It is another object of the invention to provide a process for the preparation of polymer gels that absorb C_1 to C_6 alcohols or mixtures thereof without the need for the presence of water.

Summary of the invention

Accordingly, the present invention provides a process for the preparation of polymeric absorbents useful for gelling organic liquids which comprises mixing one or more monomers with a cross-linking agent, a free radical initiator, an optional solvent, optionally in the presence of a transition metal source and subjecting the mixture so obtained to a conventional polymerisation method, removing the polymer, crushing the polymer to obtain polymer powder, washing with solvent, drying the polymer by

conventional methods to remove unreacted monomers, followed by swelling in alcohols to obtain the desired product.

In one embodiment of the present invention, the process is optionally carried out in the presence of a transition metal source.

In yet another embodiment of the invention, the source of the transition metal may be metal, metal salts or metal complexes of cobalt, chromium, copper, manganese and iron.

In a further embodiment of the invention, the transition metal source is selected from chromium trioxide, cobalt chloride, manganese hydroxide and ferric oxide.

In a further embodiment of the invention the amount of the transition metal used is between 5 ppm to 500 ppm, preferably between 10 ppm to 250 ppm.

In a further embodiment of the invention, the process is optionally carried out in the presence of a solvent.

In another embodiment of the invention, the solvent used for polymerization are polar or non-polar solvents selected from water or an aqueous mixture of alcohols, 1,4 – dioxane, dimethyl sulfoxide and dimethyl formamide, benzene and xylene.

In another embodiment of the invention, the monomers used have a general formula $CH_2=CH-R_1-R_2-R_3$ wherein R_1 and R_3 are hydrophilic groups that may be either one or a combination of amide, ester, sulfonic acid, carboxylic acid and hydroxyl functional groups, and R_2 may be a hydrophobic group chosen from one or a combination of primary, secondary or tertiary aliphatic saturated or unsaturated hydrocarbons, aromatic hydrocarbons, or cycloaliphatic hydrocarbons selected from acrylamide or their derivatives exemplified by various monomers given in Table I below:

TABLE I

Acrylamide derivative	
2-acrylamido 2-methypropane sulfonic acid N-tertiary butylacrylamide N-octyl acrylamide Acrylic acid N-propylacryamide N-isopropylacrylamide	
Ester derivative	
2-hydroxyethylmethacrylate Methylacrylate	
Copolymers	2-acrylamido 2-methylpropane sulfonic acid copolymers with N-alkylacrylamides
Amino acids	
Acryloyl – 4 – aminobutyric acid Acryloyl – 6 – aminocaproic acid Acryloyl – 11, ω – amino acid Acryloyl L – leucine Acryloyl L – glycine Acryloyl L – proline Acryloyl o – alanine	
Hydroxyl group	
Polyethylene glycols Polyethylene oxide	

In yet another embodiment of the invention, the amount of the comonomers in the polymerisation mixture may be varied between 1 mole % to 99 mole %, more preferably between 9 to 91 mole %.

In a further embodiment of the invention, the cross-linking agent may be acrylic/methacrylic or styrenic in nature or mixtures thereof and have two or more unsaturations such as N, N – methylene bisacrylamide, ethylene glycol dimethacrylate, ethylene glycol diacrylate, trimethylol propane triacrylate, trimethylol propane trimethylacrylate, divinyl benzene and more preferably N, N – methylene bisacrylamide and ethylene glycol dimethacrylate.

In a further embodiment of the invention, the mole percent of the multi-functional monomer may be typically between 0.1 mol% and 40 mol%, preferably between 1 mol% and 30 mol% and most preferably between 5 mol% and 20 mol%.

In yet another embodiment of the invention, the initiator used for thermal polymerisation is selected from azo, peroxides, hydroperoxides and persulphates, preferably from azo initiators and persulphates.

In another embodiment of the invention, tetramethyl ethylenediamine in an amount between 1 % to 4 % of the total feed is used as the polymerisation accelerator along with persulphate initiator in water as the solvent.

In yet another embodiment, the polymerisation of the polymer gel is carried out preferentially thermally between 50 to 90°C and more preferably between 50 to 70°C.

In yet another embodiment of the invention, the polymer gel may be prepared in water-alcohol mixture in the composition range of 0 to 100 volume percent of alcohol, preferably between 0 to 75 volume percent alcohol. The concentration of the monomer in solution may be varied between 5 to 50 wt. percent, preferably between 5 to 20 %.

In another embodiment of the invention, the solvent used for washing is selected from water, acetone, or an aqueous mixture of alcohols.

In a further embodiment of the invention, the polymer gel of the invention is crushed to a soft mass after polymerisation.

In another embodiment of the invention, the organic solvents include aromatics, acids, ketones, alcohols, glycols and amines.

In a further embodiment of the invention, the absorbable organic liquid is selected from aliphatic alcohols, C_1 to C_6, preferably C_1 to C_3 and more preferably C_1 to C_2.

The preferred range of modulus of the swollen polymer gel is between 0.1 to 2 MPa and a preferred range is between 0.2 to 0.6 MPa.

The gelled solvent contains 0.1 to 10 weight percent of a polymer gel, the rest being the organic solvent and/or their mixtures that are osmotically absorbed in the gel. The polymer gel contains hydrophilic and hydrophobic functional groups and is

preferably formed by polymerising a vinyl monomer having a chemical structure of the type $CH_2=CH-R_1-R_2-R_3$ wherein R_1 and R_3 are hydrophilic groups and R_2 is a hydrophobic group. The polymerisation is preferably carried out in the presence of ppm levels of a transition metal compound that can complex with the polymer.

Polymerisation can be conducted in any conventional manner. For example, polymerisation can be done by thermal polymerisation, photochemical polymerisation, solution polymerisation, bulk polymerisation, suspension polymerisation, emulsion polymerisation and precipitation polymerisation. In thermal polymerisation the initiator is activated by supplying thermal energy. Photochemical polymerisation may also be done using a radiation source.

Bulk polymerisation is carried out by dissolving the initiator in the liquid monomer. In solution polymerisation, the monomer and the initiator are dissolved in a suitable solvent in which the resultant polymer is soluble or swellable. In the case of suspension polymerisation, the insoluble monomer is suspended in water in the form of droplets with the help of a suspending agent and then polymerised.

In emulsion polymerisation, the monomer is dispersed in aqueous phase as a uniform emulsion and then polymerised. Alternatively, the resulting polymer can also be precipitated from the reaction mixture.

The separation of organic liquid from the gel by the action of temperature of pressure is not preferable. In the present invention, the organic liquid is osmotically absorbed in the gel due to the action of strong intermolecular forces. The gel does not contain macroporosity and hence the solvent cannot separate from the gel on the application of pressure. The choice of monomers also ensures that the organic solvent does not separate from the gel due to the change in temperature.

The process of the present invention will now be described with reference to the following examples, all of which are illustrative and are not to be construed as limiting the scope of the invention in any manner.

Example 1

To a well stirred solution of 1 mole of Acrylamido – 2 – methyl – propane sulfonic acid (AMPS), containing 20 ml of distilled water, 0.154 gm of N, N^1 – methylene bisacrylamide (Bis-Am), 0.04 gm ammonium persulfate (APS) and 0.06 ml tetraethylene methylene diamine (TEMED) were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 60°C for 24 hours. After the polymerisation, the polymer rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar

S. No	Polymer Gels with mole percentage of crosslinking	Swelling ratio in methanol (g/g)	Swelling ratio in ethanol (g/g)
1	PAMPS gel with 10 mole percent crosslinking	51.4	55.82
2	PAMPS gel with 20 mole percent crosslinking	16.84	18.98
3	PAMPS gel with 30 mole percent crosslinking	11.12	10.21

Example 2

To a well stirred solution of 1 mole of AMPS containing 20 ml of distilled water with 125 ppm transition metal, 0.308 gm of Bis-Am, 0.04 gm APS and 60µl TEMED were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 60°C for 24 hours. After the polymerisation, the polymer rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

S. No	Polymer Gels with mole percentage of crosslinking	Amount of transition metal	Swelling ratio in methanol	Swelling ratio in ethanol
1	PAMPS gel with 20 mole percent crosslinking	0.2 gm. $CoCl_2$	23.58	23.78
2	PAMPS gel with 20 mole percent crosslinking	0.002 gm CrO_3	31.14	29.88
3	PAMPS gel with 10 mole percent crosslinking	0.002 gm CrO_3	99.89	97.61

Example 3

To a well stirred solution of 1 mole of N – tertiary butylacrylamide (N-t-BAm) containing 23 ml dimethyl sulfoxide (DMSO), 0.1 mole of AMPS, 0.154 gm Bis-Am, 0.08 gm azobisisobutyronitrile (AIBN) were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 60°C for 24 hours. After the polymerisation, the polymer rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

Polymer gel with mole percent crosslinking	Swelling ratio in methanol (g/g)	Swelling ratio in ethanol (g/g)
N-t-BA, co-AMPS gel (1.0:0.1 mole ratio) with 10 mole percent crosslinking	352.81	389.72

Example 4

In another case, 0.1 mole of N – tertiary butylacrylamide (N-t-BAm) is dissolved in 20 ml of water by heating it at 50°C. To this well dissolved solution, 1 mole of AMPS, 0.154 gm of Bis-Am, 0.04 gm APS, 60 μl TEMED were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 70°C for 24 hours. After the polymerisation, the polymer rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

Example 5

To a well stirred solution of 1 mole of N – isopropylacrylamide (N-t-BAm) containing 23 ml 1, 4 - dioxane, 0.154 gm Bis-Am, 0.08 gm AIBN were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 60°C for 24 hours. After the polymerisation, the rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

S.No.	Polymeric networks	Swelling ratio in ethanol
1	NIPAm gel with 10 mole percent crosslinking	29.31
2	NIPAm gel with 20 mole percent crosslinking	17.22

Example 6

To a well-stirred solution of 1 mole of AMPS monomer containing 10 ml, 75:25 ethanol – water mixture, 0.154 gm Bis-Am, 0.08 gm azobisisobutyronitrile (AIBN) were added. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tube was then sealed and polymerisation was carried out at 60°C for 24 hours. After the polymerisation, the rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

Example 7

To a clear solution of 2 – hydroxy ethyl methacrylate, 0.08 gm AIBN were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 60°C for 24 hours. After the polymerisation, the rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

Example 8

To a clear solution of 1.85 gms of acryloyl 6 – aminocaproic acid containing 23 ml 1, 4 – dioxane, 0.136 ml of ethylene glycol dimethacrylate, 0.08 gm AIBN were added slowly. The contents were thoroughly mixed and the solution degassed by N_2 gas bubbling through it for 10 – 15 minutes. The tubes were then sealed and polymerisation was carried out at 70°C for 24 hours. After the polymerisation, the rod was taken out of the tube and washed with water for 24 hours, dried and then crushed in a mortar.

S.No	Polymeric networks	Swelling ratio in ethanol
1	Acryloyl-4-aminobutyric acid	15.31
2	Acrylol-6-aminocaproic acid	8.05
3	Acryloyl-1,ω-aminoundecanoic acid	12.92

Example 9

In the present invention, the modulus of the swollen PAMPS gels with different degree of cross-linking is measured by a compression test in which the gel is compressed to controlled strains (α) and the stress required for compression (σ) is recorded. The relation between the stress and the strain for a swollen polymer gel is given by

$$\sigma = \gamma kT(\alpha - 1/\alpha'^2)$$

The plot of σ versus $(\alpha - 1/\alpha'^2)$ gives the modulus as the slope of the line. A soft polymer gel has a finite modulus, which is directly proportional to the crosslink density of the gel. In the present invention the modulus of the PAMPS increases as crosslink density increases. Its non-flowing nature and finite modulus define the solid nature of the organic liquid absorbed gels.

Example 10

This example shows the heating efficiency of the polymer gel prepared by the process of the present invention. One container is placed under a chafing dish containing 2 – 3 litres of water at 25°C in the water pan portion of the chafing dish and an equal quantity of water (25°C) in the food pan. This container is heated by the aid of alcohol absorbed PAMPS gel with 10 mole percent crosslinker (Example 1), and from the thermocouples in the water pan and food pan the temperatures of water in these pans are recorded. The average data of the runs are as follows:

Temperature (°C)	Time (minutes)
25 (water pan)	0
25 (food pan)	0
68 (food pan)	30
82 (water pan)	30
91 (food pan)	45
96 (water pan)	45

Example 11

This example shows the heating efficiency of the polymer gel prepared by the process of the present invention. One container is placed under a chafing dish containing 2 – 3 litres of water at 31°C in the water pan portion of the chafing dish and an equal quantity of water (29°C) in the food pan. This container is heated by the aid of N – tertiarybutylacrylamide copolymer with AMPS, 10 mole percent crosslinker (Example 3), and from the thermocouples in the water pan and food pan the temperatures of water in these pans are recorded. The average data of the runs are as follows:

Temperature (°C)	Time (minutes)
29 (food pan)	0
31 (water pan)	0
78 (food pan)	15
89 (water pan)	15
92 (food pan)	30
97 (water pan)	30

Advantages of the invention:

The process of the invention provides a method for the preparation of slightly cross-linked polymers that are capable of absorbing organic liquids in the presence of a ppm additive. The process of the invention more particularly provides a slightly cross linked polymers that are capable of absorbing alcohols due to a balanced hydrophilic and hydrophobic character in their chemical structure.

The process being generic in nature can be extended to synthesis of gels as absorbents for various other substrates of importance.

Claims:

1. A process for the preparation of polymeric absorbents useful for gelling organic liquids which comprises mixing one or more monomers with a cross-linking agent, a free radical initiator, an optional solvent, optionally in the presence of a transition metal source and subjecting the mixture so obtained to a conventional polymerisation method, removing the polymer, crushing the polymer to obtain polymer powder, washing with solvent, drying the polymer by conventional methods to remove unreacted monomers, followed by swelling in alcohols to obtain the desired product.

2 A process as claimed in claim 1 wherein the transition metal source is selected form metal, metal salts or metal complexes of cobalt, chromium, copper, manganese and iron.

3 A process as claimed in claim 2 wherein the transition metal source is selected from chromium trioxide, cobalt chloride, manganese hydroxide and ferric oxide.

4 A process as claimed in claim 1 wherein the transition metal is used in an amount between 5 ppm to 500 ppm.

5 A process as claimed in claim 4 wherein the transition metal is used in an amount between 10 ppm to 250 ppm.

6 A process as claimed in claim 1 wherein the optional solvent used for polymerisation is a polar or a non-polar solvent selected from water or an aqueous mixture of alcohols, 1,4 – dioxane, dimethyl sulfoxide and dimethyl formamide, benzene and xylene.

7 A process as claimed in claim 1 wherein the monomers used have a general formula $CH_2=CH-R_1-R_2-R_3$ wherein R_1 and R_3 are hydrophilic groups and R_2 is a hydrophobic group.

8 A process as claimed in claim 7 wherein R_1 and R_3, comprises individually or a combination of, amide, ester, sulfonic acid, carboxylic acid and hydroxyl functional

groups, and R_2 is chosen from one or a combination of, primary, secondary or tertiary aliphatic saturated or unsaturated hydrocarbons, aromatic hydrocarbons, or cycloaliphatic hydrocarbons selected from acrylamide or derivatives thereof as shown in the Table below:

Acrylamide derivative	
2-acrylamido 2-methypropane sulfonic acid N-tertiary butylacrylamide N-octyl acrylamide Acrylic acid N-propylacryamide N-isopropylacrylamide	
Ester derivative	
2-hydroxyethylmethacrylate Methylacrylate	
Copolymers	2-acrylamido 2-methylpropane sulfonic acid copolymers with N-alkylacrylamides
Amino acids	
Acryloyl – 4 – aminobutyric acid Acryloyl – 6 – aminocaproic acid Acryloyl – 11, ω – amino acid Acryloyl L – leucine Acryloyl L – glycine Acryloyl L – proline Acryloyl o – alanine	
Hydroxyl group	
Polyethylene glycols Polyethylene oxide	

9. A process as claimed in claim 1 wherein the amount of the co-monomers in the polymerisation mixture is between 1 mole % to 99 mole %, more preferably between 9 to 91 mole %.

10. A process as claimed in claim 1 wherein the cross-linking agent is acrylic/methacrylic or styrenic in nature or mixtures thereof and have two or more unsaturations.

11. A process as claimed in claim 10 wherein the unsaturations are selected form N, N – methylene bisacrylamide, ethylene glycol dimethacrylate, ethylene glycol diacrylate, trimethylol propane triacrylate, trimethylol propane trimethylacrylate,

divinyl benzene and more preferably N, N – methylene bisacrylamide and ethylene glycol dimethacrylate.

12. A process as claimed in claim 1 wherein the mole percent of the multi-functional monomer is between 0.1 mol% and 40 mol%, preferably between 1 mol% and 30mol% and most preferably between 5 mol% and 20 mol%.

13. A process as claimed in claim 1 wherein the initiator used for thermal polymerisation is selected from azo, peroxides, hydroperoxides and persulphates, preferably form azo initiators and persulphates.

14. A process as claimed in claim 1 wherein tetramethyl ethylenediamine in an amount between 1 % to 4 % of the total feed is used as the polymerisation accelerator along with persulphate initiator in water as the solvent.

15. A process as claimed in claim 1 wherein the polymerisation of the polymer gel is carried out preferentially thermally between 50 to 90°C and more preferably between 50 to 70°C.

16. A process as claimed in claim 1 wherein said polymer gel is prepared in water-alcohol mixture in the composition range of 0 to 100 volume percent of alcohol, preferably between 0 to 75 volume percent alcohol.

17 A process as claimed in claim, 1 wherein the concentration of the monomer in solution is between 5 to 50 wt. percent, preferably between 5 to 20 %.

ABSTRACT

The invention discloses a process for the preparation of polymeric absorbents useful for gelling organic liquids. The process comprises mixing one or more monomers with a cross-linking agent, a free radical initiator, an optional solvent, optionally in the presence of a transition metal source and subjecting the mixture so obtained to a conventional polymerisation method. The polymer is removed, crushed to obtain polymer powder, washed with solvent and dried by conventional methods to remove unreacted monomers, followed by swelling in alcohols to obtain the desired product.